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UNLIKE MOLECULAR INTERACTIONS FROM VISCOSITY AND INTER-DIFFUSION

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ABSTRACT. Force constants for unlike molecular interactions for the systems H_2—CH_4, H_2—CO_2,H_2—N_2, H_2—He, $N_2-C_2H_4$ for the Lennard-Jones (12 : 6), model have been determined by combining the data on inter-diffusion coefficient and viscosity of gas mixtures. To test the appropriateness of the force constants thus determined, the available experimental data have been compared with the values of the viscosity, inter-diffusion and thermal diffusion calculated by utilising these force constants and satisfactory agreement has been obtained. From the available data it appears that the force constants, herein determined, give better agreement than those obtained from the usual combination rules.

INTRODUCTION

Considerable amount of information has been obtained for the like molecular interactions on the Lennard-Jones (12 : 6) and the exp-six potentials from the experimental viscosity and second virial coefficient data. Some other properties such as, self-diffusion (Srivastava and Madan, 1952); thermal diffusion (Srivastava and Madan, 1953); thermal conductivity (Saxena, 1955a; Srivastava 1957a) have also been utilised. Unfortunately, information regarding the unlike molecular interactions has so far been very meagre. This is mainly due to the non-availability of suitable experimental data having sufficient accuracy and temperature range.

The most suitable property for determining unlike interactions is the inter-diffusion coefficient D_{12} for, it depends, to a first approximation, only on the unlike interactions. Usually the range of temperature for these measurements is small so that it is not possible in practice to determine accurately the unlike interactions solely from inter-diffusion data. This lead Srivastava and Madan (1953) to utilise the extensive thermal diffusion data for this purpose and the method has been subsequently employed by several workers (Saxena, 1955b; Srivastava and Srivastava, 1957; Srivastava 1957b). Recently several workers (Strehlow, 1953; Bunde, 1955c; Rumpel, 1955, Srivastava and Srivastava, 1959; Srivastava, 1959) have tried to extend the temperature range of measurement of D_{12} and have utilised their data to determine unlike interactions on the Lennard-Jones (12 : 6) model. Srivastava and Srivastava (1959) have suggested a method in which the data on inter-diffusion coefficient and the viscosity of gas mixtures are

combined to determine the force parameters for the unlike interactions. The advantage of this method is that it can be used even when the inter-diffusion coefficient is known at a single temperature provided it is sufficiently accurate. In this paper the accurate inter-diffusion data available in the literature have been combined with the data on viscosity of gas mixtures to determine unlike interactions on the Lennard-Jones (12 : 6) model.

DETERMINATION OF THE PARAMETERS

The Lennard-Jones (12 : 6) potential may be written as

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \ldots \quad (1)$$

where $\phi(r)$ is the potential energy between two molecules separated by a distance r, σ is the value of r for which $\phi(r) = 0$, ϵ is the depth of the potential well. Unfortunately, the theory is not sufficiently developed to give the unlike interaction parameters in terms of like ones and it is usual to employ some empirical combination rules for this purpose. The set of rules, hitherto most successful, is the following :—

$$\sigma_{12} = 1/2(\sigma_1 + \sigma_2) \qquad \ldots \quad (2)$$

$$\epsilon_{12} = (\epsilon_1 \cdot \epsilon_2)^{\frac{1}{2}} \qquad \ldots \quad (3)$$

Relations (2) and (3) are semi-empirical and at best only approximate; it is therefore always desirable to determine σ_{12} and ϵ_{12} from the experimental data by suitable methods.

The coefficient of inter-diffusion of two gases 1 and 2 may be written, to the first approximation, in the form

$$[D_{12}]_1 = \frac{0.002628\sqrt{T^3(M_1 + M_2)/2M_1M_2}}{p\sigma_{12}^2\Omega_{12}^{(1,1)*}(T_{12}^*)} \qquad \ldots \quad (4)$$

where D_{12} is the mutual diffusion coefficient in cm²/sec, p the pressure in atmosphere, $\Omega_{12}^{(1,1)*}$ is a reduced collision integral tabulated by Hirschfelder, Curtiss and Bird (1954), and $T_{12}^* = kT/\epsilon_{12}$. M_1, M_2 are the molecular weights and T is the temperature in °K.

The viscosity of a binary gas mixture, η_{mix}, to a first approximation is given by

$$[\eta_{mix}]_1 = \frac{1 + Z_\eta}{X_\eta + Y_\eta} \qquad \ldots \quad (5)$$

where $X_\eta = \dfrac{x_1^2}{\eta_1} + \dfrac{2x_1x_2}{\eta_{12}} + \dfrac{x_2^2}{\eta_2}$

$$Y_\eta = \frac{3}{5} A_{12}^* \left\{ \frac{x_1^2}{\eta_1} \left(\frac{M_1}{M_2} \right) + \frac{2x_1x_2}{\eta_{12}} \left(\frac{(M_1+M_2)^2}{4M_1M_2} \right) \frac{(\eta_{12})^2}{\eta_1\eta_2} + \frac{x_2^2}{\eta_2} \left(\frac{M_2}{M_1} \right) \right\}$$

$$Z_\eta = \frac{3}{5} A_{12}^* \left\{ \frac{x_1^2 M_1}{M_2} + 2x_1x_2 \left[\left(\frac{(M_1+M_2)^2}{4M_1M_2} \right) \left(\frac{\eta_{12}}{\eta_1} + \frac{\eta_{12}}{\eta_2} \right) - 1 \right] + x_2^2 \frac{M_2}{M_1} \right\}$$

x_1, x_2 are the mole fractions, η_1, η_2 are the viscosities and M_1, M_2 the molecular weights of the components 1 and 2 respectively. η_{12} is the viscosity of a hypothetical gas having the molecular weight $2M_1M_2/(M_1+M_2)$. A_{12}^* is a function of the collision integrals and is temperature dependent. It has been tabulated by Hirschfelder, Curtiss and Bird (1954). Solving Eq.(4) and (5) to eliminate σ_{12} we obtain.

$$\Lambda_{12}^* = \frac{1 - \eta_{mix} \left[\frac{x_1^2}{\eta_1} + \frac{x_2^2}{\eta_2} \right] + \frac{3}{10} \frac{x_1x_2}{\eta_1\eta_2} \frac{(M_1+M_2)^2}{M_1M_2} \eta_0 [\eta_1 + \eta_2 - \eta_{mix}]}{2x_1x_2 \left(\frac{\eta_{mix}}{\eta_0} \right) + \frac{3}{5} \frac{x_1^2}{\eta_1} \left(\frac{M_1}{M_2} \right) [\eta_{mix} - \eta_1] + \frac{3}{5} \frac{x_2^2}{\eta_2} \left(\frac{M_2}{M_1} \right) [\eta_{mix} - \eta_2] + \frac{6}{5} x_1x_2} \quad \ldots (6)$$

with $$\eta_o = \frac{266.93}{0.002628} \times \frac{2M_1M_2}{M_1+M_2} \times \frac{D_{12}}{T} \times 10^{-7}$$

Thus by knowing D_{12}, η_{mix}, η_1 and η_2 at the same temperature $T°K$, A_{12}^* may be determined. From the tables the value of T_{12}^* corresponding to this value of A_{12}^* can be read and hence $\epsilon_{12/k}$ may be calculated from the relation $T_{12}^* = kT/\epsilon_{12}$ Once the value $\epsilon_{12/k}$ is fixed, σ_{12} can be determined from Eq. (4). If D_{12} data are available at several temperatures, the corresponding values of σ_{12} are determined and the mean taken.

The force parameters σ_{12}, ϵ_{12}/k obtained for the systems H_2–CH_4, H_2–CO_2, H_2–N_2, H_2–He and N_2–C_2H_4 have been recorded in table I In the table are also given for the sake of comparison the values calculated from the combination rules. It will be seen from Table I that the values of σ_{12} determined from the experimental data are always lower than those given by the combination rule. This is to be expected as the combination rule given by Eqn. (2) is expected to hold for rigid spheres only. It may also be observed that except in the case of N_2–C_2H_4, the values obtained for $\epsilon_{12/k}$ are always higher than those obtained from the combination rule.

TABLE I

Force Parameters on the Lennard-Jones (12 : 6) Model

Gas Pair	From D_{12} and η_{mix}		From combination rules		Ref. for data	
	σ_{12} Å	ε_{12}/k°K	σ_{12} Å	ε_{12}/k°K	D_{12}	η_{mix}
H_2—CH_4	3.346	71.31	3.425	67.54	(Boyd, 1951)	(Hirschfelder, 1949)
H_2—CO_2	3 429	83.37	3.482	79.54	,,	,,
N_2—C_2H_4	3.883	135.60	3.957	137.00	,,	,,
H_2—N_2	3.283	58.41	3.325	55.20	(Bunde, 1955)	(Itterbeek, *et al*, 1947)
H_2—He	2.747	21.31	2.772	20 70	(Rumpel, 1955)	(Hirschfelder, 1949)

COMPARISON WITH EXPERIMENT

In order to test the reliability of the force parameters thus determined it is necessary to see how far they reproduce the experimental data over a wide range of temperature. In table II are shown the experimental and the calculated values of D_{12} for the systems for which data are available at more than one temperature. D_{12} values have also been calculated from the combination rules. It will be seen from table II, that the force parameters determined in the present paper represent the experimental D_{12} data better than the combination rules, and this is very marked in the case of H_2–He.

TABLE II

Experimental and the calculated values of D_{12} for H_2–N_2 and H_2–He

Gas Pair	T°K	D_{12} in cm²/sec.		
		Expt.	Calc. from force parameters obtained	Calc. from combination rules
H_2—N_2	298.2	0.7385	0.7714	0.7603
	328.2	0.9079	0.9074	0.8956
	358.2	1.052	1.053	1.016
H_2—He	298.2	1.550	1.539	1 665
	328.2	1.843	1.805	1.940
	358.2	2.080	2.092	2.232

In table III are shown the experimental and the calculated values of the viscosity of gas mixtures, η_{mix}, for different gas pairs.

In table IV are shown the calculated and the experimental values of the thermal diffusion factor k_T for the gas pairs for which data are available

TABLE III

Experimental and calculated values of $\eta_{mix} \times 10^7$ (in gm/cm.sec)

Gas Pair	T°K	% of lighter constituent	$\eta_{mix} \times 10^7$ Expt.	Calc. from force parameters obtained	Calc. from combination rules
H_2—CH_4	293	28.08	1099	1107	1093
		48.55	1098	1108	1092
		60.22	1086	1092	1081
		92.23	955	960	944
	373	28 08	1337	1339	1330
		48.55	1328	1327	1320
		60 22	1306	1307	1296
		92.23	1132	1130	1121
	473	28.08	1602	1601	1591
		48.55	1587	1574	1576
		60 22	1551	1551	1540
		92.23	1338	1329	1321
	523	28.08	1718	1722	1705
		48 55	1699	1695	1683
		60 22	1662	1663	1650
		92.23	1423	1413	1411
H_2—CO_2	300	19.93	1501	1504	1502
		41.29	1506	1510	1512
		78.50	1370	1372	1374
	400	19.93	1945	1953	1945
		41.29	1933	1938	1936
		78 50	1713	1721	1718
	500	19.93	2358	2350	2346
		41.29	2321	2318	2307
		78.50	2026	2023	2011
	550	19 93	2542	2549	2528
		41.29	2506	2515	2481
		78.50	2173	2175	2160

TABLE III (*contd.*)

Gas Pair	T°K	% of lighter constituent	$\eta_{mix} \times 10^7$		
			Expt.	Calc. from force parameters obtained	Calc. from combination rules
H_2—N_2	291.1	84.0	1251	1254	1256
		55.9	1560	1563	1567
		38 0	1660	1661	1665
		24.1	1677	1675	1679
		13 4	1742	1745	1752
H_2—He	293	55 20	1317	1319	1322
		60.69	1252	1258	1265
		69.18	1166	1172	1176
	373	55 20	1551	1550	1550
		60.69	1478	1481	1486
		69 18	1383	1379	1388
	473	55 20	1817	1818	1793
		60 69	1728	1737	1714
		69.18	1619	1617	1598
	523	55 20	1939	1942	1895
		60.69	1852	1857	1819
		69.18	1732	1735	1694
N_2—C_2H_4	300	23.79	1169	1174	1172
		43.05	1308	1312	1302
		75 95	1574	1576	1573
	400	23.79	1491	1496	1490
		43.05	1655	1658	1651
		75.95	1956	1954	1950
	500	23.79	1786	1788	1778
		43.05	1963	1974	1962
		75.95	2292	2297	2285
	550	23.79	1921	1927	1908
		43.05	2108	2117	2092
		75 95	2453	2459	2439

A glance at the Table III shows that the agreement between the experimental and the calculated values of η_{mix} is very satisfactory. In general the same degree of agreement is obtained with the force parameters determined in the paper and with those determined from combination rules. But at least in some cases the former gives better agreement.

Agreement in the case of thermal diffusion factor is only approximate. However, generally the agreement is better than that obtained with the usual combination rules. A part of the disagreement between the experimental and the calculated values of k_T may be attributed to comparatively large inaccuracy in the experimental determination of k_T.

TABLE IV

Experimental and calculated values of thermal diffusion factor k_T

Gas Pair	% of lighter constituent	T°K	$k_T \times 10^2$ Expt.	Calc. from force parameters obtained	Calc from combination rules	Ref. for data
H_2—CO_2	53	300	6.89	8 13	8.39	(Bastick *et al*, 1939)
		370	8.99	8 89	9 60	
H_2—N_2	29.4	143	3.95	4.07	3.97	(Ibbs *et al*, 1926)
	42.0		5.21	5.23	5.01	
	77.5		4.84	4 92	4.44	
	29 4	264	5 48	5 74	5 90	
	42.0		7 49	7.39	7.37	
	77 5		6 63	7.04	6.36	
H_2—He	81	358	1.79	2 05	2.31	(Murphey, 1947)
	50	330	4.81	3 94	3.74	(Heath, 1941
	60		4.42	3.88	3.56	
	70		3 50	3.38	3 08	
	80		2 84	2 62	2.31	
	90		1.32	1.44	1.29	

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